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During this reporting period, we have made progress in the deposition and characterization of novel nanometer-layered yttna/zirconia coatings. Fully oxidized Y_2O_3/ZrO_2 superlattices of bilayer thicknesses Λ ranging from 2 nm to 100 nm have been deposited at high rates of ≈3.4 μm/hour, or 70% of the pure metal rates. The superlattices were structurally characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The ZrO_2 layer exhibited its high temperature ($\geq$ 2400 °C) cubic-fluorite structure at small layer thickness $\leq$ 7 nm, epitaxially stabilized by the cubic Y203. The mechanical properties of the superlattices were measured using a nanoindenter and the thermal conductivity measurements by the 3ω method. The optical properties of oxides of Al, Y, Zr, and Y_2O_3/ZrO_2 superlattices was investigated using spectroscopic ellipsometry. In addition, the thermal stability of the superlattices was investigated.

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Progress Report
August 1, 1997 – July 31, 1998

Synthesis and Characterization of Oxide Superlattice Coatings

Principal Investigator: Scott A. Barnett

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Progress Report

Synthesis and Characterization of Oxide Superlattice Coatings

Status of effort

During this reporting period, we have made progress in the deposition and characterization of novel nanometer-layered yttria/zirconia coatings. Fully oxidized Y_2O_3/ZrO_2 superlattices of bilayer thicknesses Λ ranging from 2 nm to 100 nm have been deposited at high rates of $\approx$ 3.4 μm/hour, or 70% of the pure metal rates. The superlattices were structurally characterized using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The ZrO_2 layer exhibited its high temperature ($\geq$ 2400 °C) cubic-fluorite structure at small layer thickness $\leq$ 7 nm, epitaxially stabilized by the cubic Y_2O_3. The mechanical properties of the superlattices were measured using a nanoindenter and the thermal conductivity measurements by the 3ω method. The optical properties of oxides of Al, Y, Zr, and Y_2O_3/ZrO_2 superlattices was investigated using spectroscopic ellipsometry. In addition, the thermal stability of the superlattices was investigated.

Accomplishments/New Findings

Deposition of polycrystalline Y_2O_3/ZrO_2 superlattices

Various aspects of process control required to deposit monolithic oxide coatings at high rates have been described in previous reports. Simultaneous reactive sputtering from two targets presents special challenges for process control, since both deposition rates are sensitively dependent upon oxygen partial pressure. The superlattices were deposited in a new opposed cathode unbalanced magnetron sputtering system – the details have been described in previous reports. Figure 1 shows the hysteresis curves for reactive sputtering of Y and Zr targets. Both targets show a pronounced negative-slope region, which is where high deposition rates and fully oxidized films are obtained. The Y-O_2 has a larger negative region. In this region, the Y target is making the transition from sputtering in metallic mode to the oxide mode. Since the rates depend sensitively on P_{O2}, accurate P_{O2} control is needed to obtain reproducible and uniform superlattice layer thicknesses. We typically use partial-pressure control techniques to ensure stable deposition

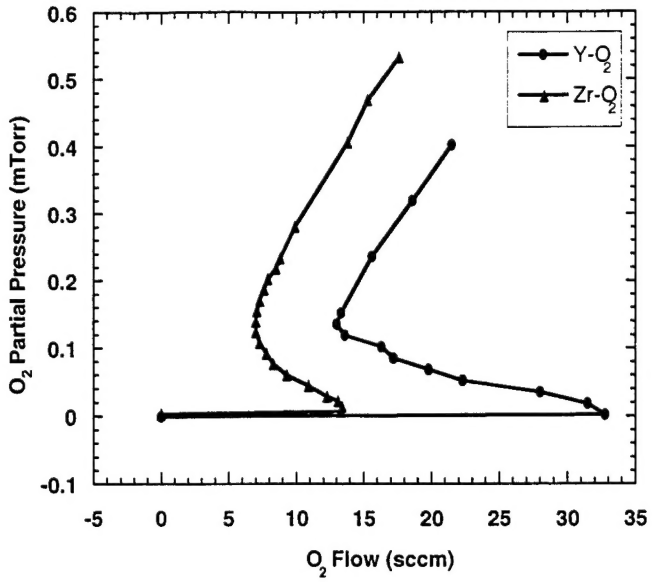

Figure 1: O_2 partial pressure vs. O_2 flow rate for Y-O_2 and Zr-O_2 with a total Ar pressure of 4 mTorr and target powers of 3 kW for the Y and 1.5 kW for the Zr.

rates, and hence well-controlled superlattice layer thicknesses. However, for Y and Zr targets, it was found that the mass spectrometer signal was not accurate enough to provide the desired film-thickness reproducibility. To handle this problem, the Y target voltage was used to control the O_2 partial pressure. The voltage decreases rapidly as oxides begin to form on the surface of the target, providing a very sensitive control signal for the O_2 partial pressure.

Structural characterization

X-ray diffraction (XRD) was done using a SCINTAG XDS 2000 PAD diffractometer with CuKα radiation, operated at 40 kV and 40 mA. Figure 2 shows an example of the high-angle x-ray diffraction pattern obtained from an as- deposited $\Lambda = 8.6$ nm superlattice, along with results obtained after annealing. The superlattices show both cubic-(222) and cubic-(440) reflections, along with Si substrate peaks and a $Y_2Si_2O_7$ peak due to a film/substrate reaction at the interface. In the as-deposited films there is substantial lattice disorder, due to the low deposition temperature and ion bombardment, such that the peaks are broadened. After annealing, the disorder is decreased substantially, as shown for example for 1100°C in Fig. 2, where the peaks have sharpened significantly. Note that at the c-(440) peak, a superlattice Bragg peak along with positive and negative satellites are present.

The observation of only cubic ZrO_2 peaks is in agreement with TEM data, and is explained as follows. Pure Y_2O_3 exhibits a cubic structure with a lattice parameter of 1.06 nm. Pure ZrO_2 can

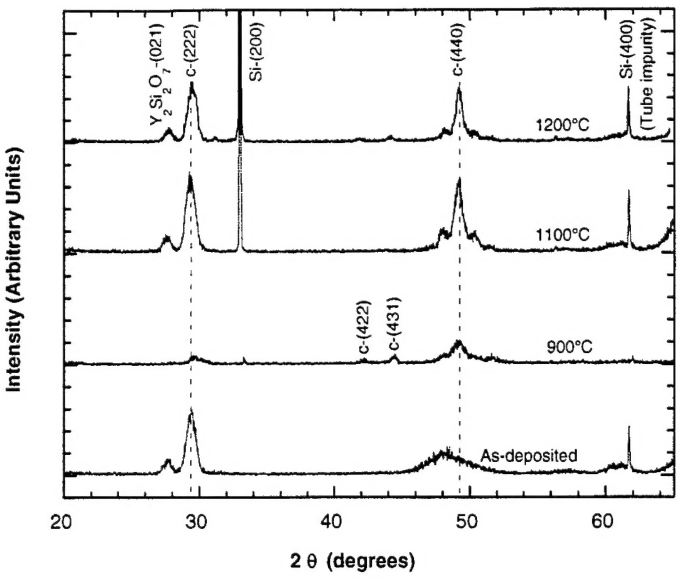

Figure 2: X-ray diffraction patterns from as-deposited and annealed Y_2O_3/ZrO_2 superlattices (period = 8.6 nm).

exist in monoclinic (stable below ~ 1200°C), tetragonal (1200°C to 2300°C), and cubic (>2300°C) structures. Two unit cells of cubic ZrO_2, with a lattice parameter of 0.51 nm, match well (3.8% mismatch) with one unit cell of Y_2O_3. On the other hand, the monoclinic and tetragonal structures cannot easily form coherent interfaces with yttria. Previous work has shown that non-equilibrium structures crystallize in superlattices, where interfacial areas are large, in order to form low-energy interfaces. Pseudomorphic layers have been observed in a few nitride superlattices previously, including AlN/TiN and CrN/TiN. In both cases, the TiN layers help stabilize cubic forms of the other layer, as opposed to the stable hexagonal structures, and high hardness values are achieved.

Thermal stability

Our recent results for yttria/zirconia superlattices show that superlattices with nanometer-thick layers can possess remarkable stability. Figure 3 shows x-ray reflectivity results for different annealing temperatures from a superlattice with Λ = 8.6 nm. These results when compared with simulations indicate only a very slight change in the superlattice structure up to ≈ 1100°C, and some intermixing and/or layer roughening at 1200°C, the highest temperature measured. This result agrees well with the high-angle XRD superlattice reflections (Fig. 2) that decrease in intensity at 1200°C. This good stability is somewhat surprising given that the yttria-zirconia phase diagram indicates considerable solid solubility, and the possible formation of a

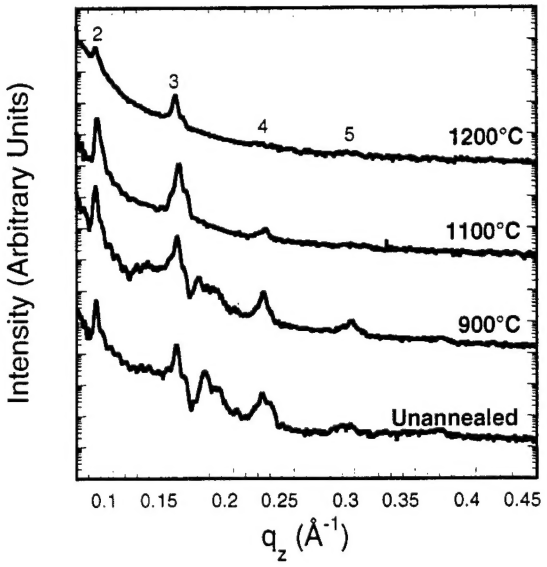

Figure 3: X-ray reflectivity results for different annealing temperatures for a Y_2O_3/ZrO_2 superlattices.

ternary compound. Other systems that are fully immiscible, e.g. alumina/zirconia, presently under investigation, should be even more stable in superlattice form.

Mechanical properties

The mechanical properties of yttria-zirconia superlattices were investigated using a UMIS nanoindenter. The nanoindenter loading-unloading curves were qualitatively similar to those for pure zirconia and yttria films. Figure 4 shows the hardness vs. period obtained for yttria/zirconia, pure yttria, and zirconia. Two series of films were deposited with layer thickness ratios of t_{Y2O3}/Λ

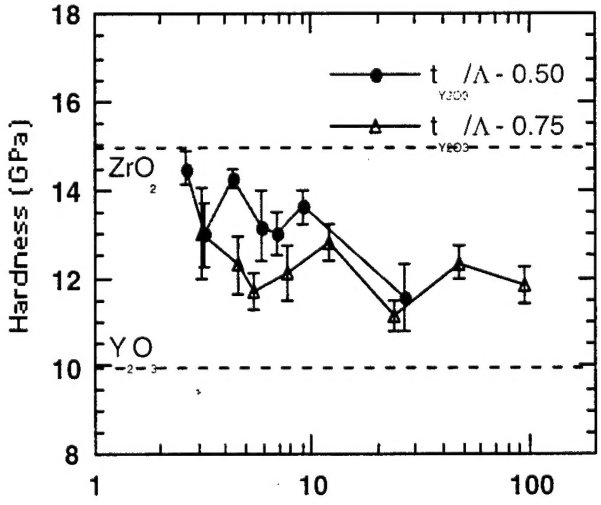

Figure 4: Hardness of Y_2O_3/ZrO_2 superlattices as a function of superlattice period. Two different layer thickness ratios of $t_{Y2O3}/\Lambda \sim 0.50$ and $t_{Y2O3}/\Lambda \sim 0.75$ are shown.

= 0.75 and 0.5. The hardness was 11 - 12 GPa at large periods, where the hardness typically approaches the rule-of-mixtures value. The hardness generally increased with decreasing period, reaching 14.5 GPa at the smallest period measured. This represents a hardness enhancement of ≈20% relative to rule of mixtures values. The results in Fig. 4 are in agreement with prior superlattice results, which typically show hardness increasing with decreasing period.

Thermal conductivity

There is considerable experimental and theoretical evidence of substantial κ reductions in semiconductor superlattices with nm layer thicknesses. The results are typically explained in terms of decreases in the phonon mean free path and/or reduced phonon velocities. The thermal conductivity of the Y_2O_3/ZrO_2 superlattices was measured using a 3ω technique developed by David Cahill at University of Illinois at Urbana-Champaign. Figure 5 shows a 30-40% reduction in

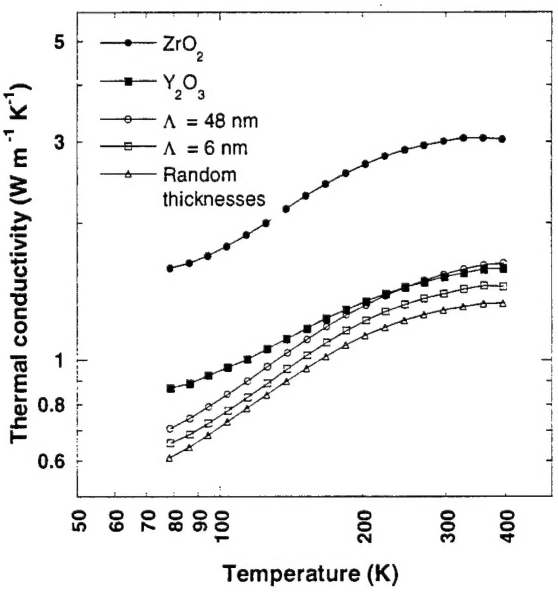

Figure 5: Thermal conductivity of Y_2O_3/ZrO_2 superlattices for periods 6 nm and 48 nm. The thermal conductivity of pure ZrO_2 and Y_2O_3 is also shown.

κ in yttria/zirconia superlattices compared to rule-of-mixtures values. While much more work is needed, particularly κ measurements at higher temperatures, this result suggests exciting new engineering applications.

Optical Properties

Oxides of Al, Y, Zr and Y_2O_3/ZrO_2 superlattices were deposited using a 13.56 MHz Advanced Energy rf power supply was used to bias the substrates. The optical properties were investigated as a function of the bias. Spectroscopic ellipsometry showed that the index of

refraction of the films deposited with a substrate bias of 80 V (dc component) were equal to that of the bulk materials. The optical constants of Y_2O_3/ZrO_2 superlattices with $\Lambda \leq 25$ nm were as expected by taking a weighted average of Y_2O_3 and cubic ZrO_2 suggesting that the ZrO_2 layers were epitaxially stabilized by the Y_2O_3 layers. For $\Lambda \geq 25$ nm, the optical constants were equal to the weighted average of Y_2O_3 and monoclinic ZrO_2 indicating a structure change as the ZrO_2 layer reaches a critical thickness. Work is ongoing to deposit alumina/zirconia coatings and optimize the deposition parameters to obtain transparent films.

Future work

With the deposition of nanometer-layered yttria/zirconia coatings, we have been able to demonstrate that it is possible to deposit nanometer scale oxide multilayers at high deposition rates in a well-controlled manner. With our understanding of the effects of process parameters on the structure and properties of the reactively sputtered oxide films, we are now in an excellent position to study many novel oxide multilayer systems. Work is ongoing to deposit alumina/zirconia and alumina/chromia coatings. The superlattice systems to be studied will provide enough data to understand the key materials parameters that influence superlattice properties. We believe that these experiments will unambiguously answer fundamental questions as to the effect of nano-phase composite structure on hardness and thermal conductivity, and provide new materials with interesting new properties.

Personnel Supported

Personnel supported on this program are Professor Scott A. Barnett, Dr. Michael Graham, Mr. Tony Lefkow, Dr. Phil Yashar, Dr. Anita Madan, Mr. Pat Doherty and Keith Martin. Phil Yashar completed his Ph.D on this project. A current graduate student, Keith Martin, has worked for about 1 year on this project.

Publications

The publications associated with this work published or accepted for publication over the past year are:

1. P. Yashar, J. Rechner, W. D. Sproul, and S. A. Barnett, Structure and mechanical properties of polycrystalline CrN/TiN superlattices, J. Vac. Sci. Technol. A (accepted).

2. J.M. Schneider, W.D. Sproul, A. Matthews, "Reactive ionized magnetron sputtering of crystalline alumina coatings," Surface & Coatings Technology 98(1-3), 1473 (1998).

3. J.M. Schneider, W.D. Sproul, R.W.J. Chia, M.S. Wong, "Very-high-rate reactive sputtering of alumina hard coatings," Surface & Coatings Technology, 96(2-3), 262 (1997).

4. J.M. Schneider, W.D. Sproul, A. Matthews, "Phase formation and mechanical properties of alumina coatings prepared at substrate temperatures less than 500 degrees C by ionized and conventional sputtering," Surface & Coatings Technology 94-5(1-3), 179 (1997).

5. J.M. Schneider, W.D. Sproul, A.A. Voevodin, A. Matthews, "Crystalline alumina deposited at low temperatures by ionized magnetron sputtering," Journal Of Vacuum Science & Technology A-Vacuum Surfaces And Films, 15(3), 1084 (1997).

6. P. Yashar, J. Rechner, M. S. Wong, W. D. Sproul, and S. A. Barnett, High-rate reactive sputtering of yttria-stabilized zirconia using pulsed d. c. power, Surf. Coat. Technol. **94-95**, 333 (1997).

Interactions/Transitions

Presentations (Invited talks are represented by *)

1. *A. Madan, *Engineered Nanolayered Composites,* Ford Research Institute, Detroit, MI, July 1998.

2. P. Yashar, A. Lefkow, and S. A. Barnett, *Optical Properties of Sputtered Oxide Materials*, International Conference on Metallurgical Coatings and Thin Films, San Diego, April 1998.

3. *S. A. Barnett, A. Madan, I. Kim, and P. Yashar, *Reactive Sputtering of Nanometer-Scale Multilayer Coatings*, International Conference on Metallurgical Coatings and Thin Films, San Diego, April, 1998.

4. *A. Madan, *Coatings-by-design*, Surface Engineering Group Meeting, National Institute of Standards and Technology, Gaithersburg, MD, April 1998.

5. *A. Madan, *Engineered Nanolayered Composites,* "Advanced and Emerging PVD/CVD Coating Technologies, Case Studies, and New Industrial Applications" – Workshop instructor - Wear and Superhard Coatings Conference, Tampa, FL, March 1998.

6. P. Yashar, W. D. Sproul, L. Hultman, and S. A. Barnett *Deposition and mechanical properties of polycrystalline Y_2O_3/ZrO_2 superlattices*, Materials Research Society Meeting, Boston, December 1997.

7. P. Yashar, W. D. Sproul, and S. A. Barnett *Deposition and properties of polycrystalline Y_2O_3/ZrO_2 superlattices*, McNU Meeting, Evanston, August 1997.

Patents

"Multilayer oxide coatings" Sproul, William D., Barnett, Scott A., Lefkow, Anthony, Wong, Ming-Show, Yashar, Philip

Patent # 5789071

"Method for magnetron sputtering alumina and other compounds onto a substrate" Schneider, Jochen, Sproul, William D.

Patent pending